

Development and Evaluation of a New Liquid Cell System for Soft X-Ray Absorption Experiments

S. Matsuo¹, T. Kurisaki², H. Yamashige², P. Nachimuthu³, R. C. C. Perera⁴, and H. Wakita^{1,2}

¹Advanced Materials Institute, Fukuoka University, Nanakuma, Jonan-ku, Fukuoka 814-0180, Japan

²Department of Chemistry, Faculty of Science, Fukuoka University,
Nanakuma, Jonan-ku, Fukuoka 814-0180, Japan

³Department of Chemistry, University of Nevada Las Vegas, Las Vegas, NV 89154-4003, USA

⁴Center for X-ray Optics, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

INTRODUCTION

The light of the soft X-ray region is well used as a means available to investigate the electron state of valence band in a material, because the energy of the soft X-ray light is close to that of the valence band and strongly affects the material. A soft X-ray absorption spectrum provides information on the electron states of an absorbing atom and between the absorbing atom and neighboring atom(s) in a material, in addition, the researches with the soft X-ray absorption spectroscopy are extensively developed with the increase of the number of the target atoms for the researches, because the elements absorbing the soft X-ray light include not only the light elements, but also the elements which can cause the L- and M-shells excitation. So far, for solid samples, the soft X-ray absorption spectroscopy has been, in fact, utilized for the results and developments for functional materials, the speciation of pollution compounds, the understanding of mechanism for catalytic reactions and vital functions [1]. However, the soft X-ray absorption experiments for liquid samples have been much hard to need the precise design of the liquid cell system possible for the experiments under atmospheric pressure plus the reduction of the incident beam intensity. In this paper, we report on a new liquid cell system for the soft X-ray absorption experiments developed at ALS, and show the X-ray absorption near-edge structure (XANES) spectra for aqueous Al salt solutions by the use of the cell system.

APPARATUS

The setup of the developed cell system is depicted in Figure 1. This cell system connects with the reflectometer of the endstation in BL6.3.1, and has the vacuum system with two shutters to keep the pressure in the path, ca. 10^{-7} Torr. Only a silicon nitride (Si_3N_4) membrane, which has thickness of 150 nm and dimensions of 1 mm square with surrounding silicon support with thickness of 0.38 mm and dimensions of 5 mm square, is fixed on the end of the pressure path. A liquid sample is trapped between two other Si_3N_4 membrane windows, on which the microspheres (ca. 10 μm in diameter) of polystyrene are dropped in advanced. The liquid sample trapped is fixed on the sample holder, which is made of stainless and designed as the beam is transmitted by the sample liquid and detected by the silicon photodiode under the optimal condition, and then it is put on the sample stage. The end of the pressure path, sample stage, and detector are covered with the acryl case.

EXPERIMENTAL

Aluminum K-edge XANES spectra were collected by a transmission mode using the cell system for samples of aqueous solution and by a total electron yield method for powder samples pressed onto conductive carbon tape. The measured aluminum compounds were aluminum chloride

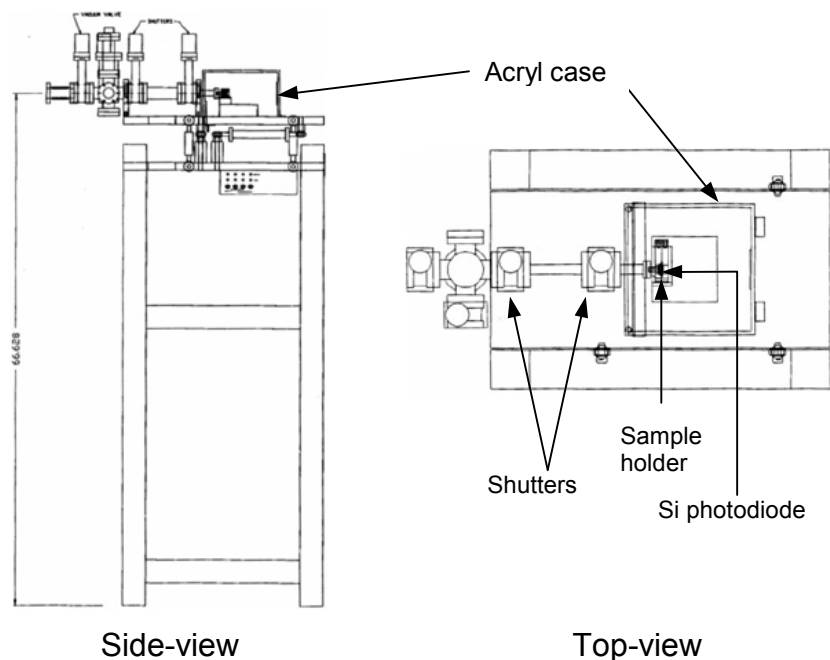


Figure 1. New liquid cell setup for soft X-ray absorption spectral measurements for solutions.

(AlCl_3), aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), sodium aluminate (NaAlO_4), and aluminum ethylenediaminetetraacetate (Al-EDTA) complex. The Aqueous solution of Al-EDTA was prepared by adding 0.5 M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ aqueous solution (25 ml) to 0.5 M EDTA tripotassium salt aqueous solution (25 ml) and finally adjusted to pH 4.5 and the powder was purchased from Dojin, Al-EDTA sodium salt dihydrate. The others were high-concentrated aqueous solutions. Data were collected from 1550 to 1620 eV at intervals of 0.2 eV with the speed of 0.5 s a point. In the measurements, He gas was made to flow and to fill in the acryl case, which was covered with a black cloth.

RESULTS

The Al K-edge XANES spectra for the aqueous solutions of AlCl_3 , $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, NaAlO_4 , and Al-EDTA are shown in Figure 2 with those for the powder of them. In the powder samples, all the peak tops of the XANES spectra appear in almost similar energy position. In the aqueous solution samples, on the other hand, the peak tops of the XANES spectra of AlCl_3 and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ are similar in the position to those in their powder samples, while those of NaAlO_4 and Al-EDTA are different from those in their powder samples, and shift to the low energy side. These results indicate that the coordination numbers for AlCl_3 and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ little change between the powder and aqueous solution, and those for NaAlO_4 and Al-EDTA change. In fact, the coordination number

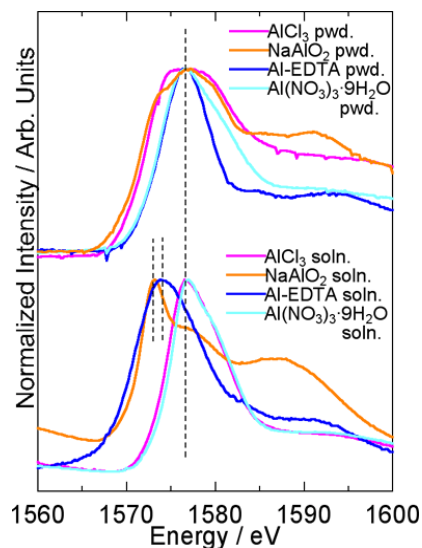


Figure 2. Al K-edge XANES spectra for Al compounds in solid state and in aqueous solution.

of Al-EDTA has been proposed to be six and five in powder and aqueous solution from NMR experiments, respectively [2]. Accordingly, the peak position of the XANES spectra for Al-EDTA can be related with the coordination number. Furthermore, the relation between the peak position and coordination number would be also applied for all aluminum compounds.

CONCLUSION

The new liquid cell system for the soft X-ray absorption experiments developed at ALS enabled us to record the spectra characteristic of chemical species in solution. For the XANES spectra of aqueous aluminum salt solutions obtained by the liquid cell system, the change of the peak position was related with the coordination structure, especially coordination number.

REFERENCES

1. H. Wakita, Bunseki (in Japanese) **1**, 24 (2002).
2. T. Yokoyama, Y. Tsuji, T. Kurisaki, and H. Wakita, presented at the IUPAC International Congress on Analytical Sciences 2001, Waseda University, Tokyo, Japan, 2001 (unpublished).

This work was supported by the Advanced Materials Institute, Fukuoka University and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Principal investigator: Hisanobu Wakita, Advanced Materials Institute and Department of Chemistry, Faculty of Science, Fukuoka University. Email: wakita@fukuoka-u.ac.jp. Telephone: +81-92-801-8883.